

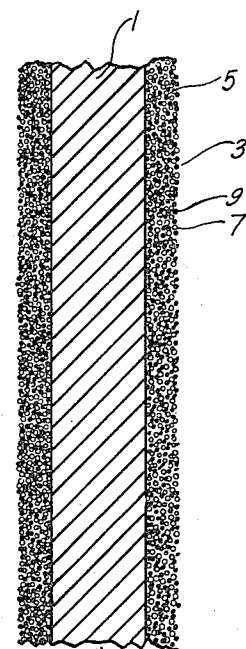
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COATED ELECTRODE

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MOLYBDENUM — • — 9

ZIRCONIUM — • — 7

MOLYBDENUM BASE

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COATED ELECTRODE

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This invention relates to electrodes for use in thermionic tubes and similar devices and particularly to the electrodes used as anodes in such devices.

It is well known that the performance of thermionic tubes may be improved by using anodes which have been coated with powdered zirconium. Two advantages are gained by the use of such coatings; first, zirconium powder has a strong affinity for gases remaining after the pumping of the tube is completed, and "flashed" or heated to a high temperature after the tube is sealed off from the pump, exercises a strong gettering action. Second, the zirconium coating is dark in color and increases the thermal emissivity of the anodes, particularly in the red and infra-red range, so that the coated anodes operate at a lower temperature than would otherwise be the case. This latter effect improves the operation of the tubes in several related ways. Viewed from one aspect it increases the overall power rating of the tube, since such rating is usually dependent upon the amount of energy which can be dissipated from the anode through radiation. Probably more important is that when the tube is operating at normal power, below the maximum rating, all of the electrodes within it, with the exception of the emitting cathode, will operate at a lower temperature. This reduces the tendency of the tube as a whole to release adsorbed gases, and also reduces the tendency of grid structures to emit primary electrons, which interfere with proper functioning of the device.

A number of methods have been proposed for improving the effectiveness of zirconium coatings. The prototype of all such coatings is one consisting of substantially pure zirconium powder suspended in a vehicle and sprayed onto the metal sheets from which the anodes are formed, either before or after such formation. The vehicles used most commonly are colloidal silicates or pyroxylin lacquers and act not only to carry the metallic powder during the spraying operation but also as binders to cement the powder to the metal backing. Various suggestions have been made looking to the improvement of one or the other of the functions of the zirconium coating without reducing its effectiveness in performing its other function. Typical of such suggestions is the Widell Patent No. 2,536,673, which covers the admixture of a small percentage of zirconium oxide with the metallic powder for the purpose of preventing the alloying of the zirconium with the metal base, and the consequent loss of gettering action, while still maintaining

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a reasonably good thermal bond and a correspondingly high radiation coefficient.

The instant invention falls generally into the class of improvements upon zirconium coated electrodes. Included among the objects of the invention are to provide an electrode having an even higher emissivity or coefficient of radiation than that of pure zirconium powder, to provide a coated electrode having a close thermal bond between the coating and the metal base, and, as a result of these two properties, to provide an electrode which, for a given surface area, will dissipate more power at a given temperature or operate at a lower temperature for a given power input than will other electrodes of the same general class and which will, at the same time, retain the advantages of the gettering action of zirconium coatings.

Considered broadly the electrode of this invention comprises a base of sheet molybdenum. Applied to the base is a mixture of powdered zirconium and powdered molybdenum, suspended in a suitable vehicle or binder such as a hydrolyzed ethyl silicate or tetra-ethyl ortho-silicate. The percentage of the components of the powder mixture is not critical. The zirconium metal should be present in the proportion of at least fifty percent and experience has indicated that the best proportion for most purposes lies between seventy-five and eighty percent of zirconium, but the addition of molybdenum powder to the zirconium in any degree increases the radiation coefficient and hence is of advantage.

The single figure of the drawing is an enlarged diagrammatic sectional view of a portion of an electrode structure, coated in accordance with the present invention.

Because of the rapid deterioration of the coating when exposed to the oxidizing action of the air or to moisture from the hands of operators, the mechanical operations involved in making the electrodes, with the exception of the final mounting thereof in the tubes, are performed prior to applying the zirconium-molybdenum coating. The base on which the coating is applied should be as nearly chemically clean as is possible of achievement. Any treatment which will secure chemical cleanliness is suitable. It is also desirable that the base material have a mat or very slightly roughened surface and among the treatments suitable for both cleansing and roughening the surface is sand blasting. It is to be understood that the invention resides in the ultimate nature of the coated electrode rather than in the steps employed in applying the coat-

ing and in the description of the formation of the coating which follows the steps described as employed are illustrative only and indicative of the precautions to be taken in forming it rather than as limitations affecting the final nature of the coated plates. Equivalent steps, which will achieve the same results as far as cleanliness and the nature of the surface are concerned, may be substituted without affecting the final product.

In accordance with the preferred method of forming the coating the mechanically completed electrodes, which may, for example, be cylindrical anodes for vacuum tubes of almost any type, are first placed in a lead beaker or similar vessel and immersed in commercial hydrofluoric acid, undiluted. An alternating potential of the order of thirty volts is then applied between the anodes and the beaker for a period of from two to three minutes. This treatment not only removes any oil, dirt, or grease which may have been gathered by the surface of the molybdenum electrodes during their fabrication, but also etches the surface, leaving a white mat finish which makes sand blasting unnecessary. During this step of the operation the utmost precautions are taken to prevent injury to the operators by the acid or its fumes. The treatment is carried out under an exhaust hood and the workers all wear elbow length rubber gloves in order to protect the skin from both fumes and possible droplets of the powerful acid.

The electrodes are next rinsed very thoroughly in running water and finally boiled in distilled water to remove the last possible traces of acid or salts derived either from the acid bath or from the undistilled water in which they are rinsed. Following this they are air dried and are then ready for the spraying operation.

The coating with the mixed powders of zirconium and molybdenum is normally applied by spraying with the powders suspended in a vehicle of a hydrolized organic silicate. Of such products ethyl-silicate or tetra-ethyl ortho-silicate are the most readily available. Various formulas for preparing the vehicle are obtainable from the manufacturers thereof and substantially any of these formulas may be used. One which has proved satisfactory in practice is as follows:

- I. 200 cc. ethyl-silicate
100 cc. denatured alcohol (shellacol, methanol)

Stir with motor agitation.

- II. Add: 30 cc. 1% hydrochloric acid, stir.

This formula provides slightly more water than is necessary to hydrolize the silicate and also provides a slightly higher acidity than is necessary to prevent the formation of a gel with such rapidity that the vehicle cannot be used satisfactorily. Complete hydrolyzation can be secured if the amount of 1% acid be reduced by one-third, to 20 cc., and the amount of acid will still be sufficient to prevent immediate gelling. It has been found, however, that the excess water and acid do no harm and extend the period for which the vehicle is usable.

The mixed powders of zirconium and molybdenum are then added to the colloidal solution prepared as above. The zirconium is always handled moist, since it is extremely reactive to oxygen and is liable to spontaneous combustion. Although, as has been stated, there is a wide range of mixtures which may be employed, the preferred formula employs sixty parts by weight of the moist zirconium and seventeen parts by

weight of molybdenum or 78 percent of zirconium and 22 percent of molybdenum. Actually the fact that moist molybdenum powder is used will upset these proportions very slightly, but the water content of the moist powder is relatively small and the density of the zirconium powder is high—approximately 6.4 and hence the actual percentages of the constituents is very nearly that given. As the relative percentages are not critical in any event this becomes a matter of no importance.

The mixture of powdered metals is added to the vehicle, and the whole is well stirred. Finally an additional 170 cc. of denatured alcohol is added and thoroughly mixed by rolling in a paint mill until ready for use. The quantity of the vehicle employed per gram of metal powder depends very largely upon the spraying equipment. It is possible to apply a spray with as little as 1 cc. of vehicle per gram. Satisfactory coats have been produced with approximately 6 cc. of vehicle per gram. Ordinarily a value intermediate these two extremes will be used.

The coating is applied, as has been indicated, by ordinary spray gun equipment. After the electrodes are sprayed, inside and out, they are again air dried. Experience has shown that undue oxidation does not occur if this final drying process is carried out in a dry oven or "hot box" at a temperature not exceeding 100° C. for a period of six to eight hours.

When the drying is complete the electrodes are placed in a vacuum furnace and sintered at a temperature of approximately 1600° C. An important point with respect to this part of the process is that it be carried out in as good a vacuum as it is possible to maintain in the furnace. Too low a vacuum is indicated by the surface appearing colored instead of dead black. The plates should be cooled to substantially room temperature before they are exposed to the oxygen of the air. After the sintering operation the zirconium content of the coating is highly activated and oxidation occurs rapidly. The electrodes should be mounted within the tube, and the latter evacuated and sealed off as soon as possible. The electrodes should not be stored in or exposed to the temperature of a hot box pending the evacuation and sealing off process, and it is advantageous that all operations requiring an elevated temperature be carried on in an atmosphere of inert gas, such as pure nitrogen.

The resultant structure is illustrated diagrammatically in the drawing. The molybdenum base 1 is covered on each side with an adherent coating 3 formed as described. An attempt is made in the upper portion of the figure to indicate the structure of this coating, which comprises a silica matrix 5 in which are imbedded particles 7 of zirconium and 9 of molybdenum. The silica matrix is a substantially pure silica gel, is highly porous, and permits access of residual gas in the tube to the zirconium getter.

The resultant coatings 3 differ substantially from those of the prior art only in that they contain the particles of molybdenum interspersed with those of zirconium. The effect of this coating is, however, unexpected in view of prior art teachings. Widell, for example, has indicated that the tendency of zirconium to alloy with the base material materially reduces the gettering action, but within the limits of error of available experimental techniques it has been found that the gettering action of zirconium in the coating of the present invention, considered in terms

of the amount of gas adsorbed, is what would be expected from the actual amount of zirconium employed. This is in spite of the fact that molybdenum is one of the most widely used base materials and in the present invention the zirconium powder is intimately mixed with molybdenum and hence, from the teachings of the prior art, a high degree of alloying might be expected. It is also in spite of the fact that no additive is used to prevent alloying.

The great advantage of the coating herein described lies in its increased "blackness." The density of molybdenum is approximately 40 percent greater than that of zirconium, and hence, by volume, of the proportions of the two metals specified in the formula given above the molybdenum comprises less than 17 percent of the mixture. Nevertheless, the molybdenum powder, considered as a pigment, has great covering power and the coating produced in accordance with this invention has a higher coefficient of radiation and approaches much more closely the ideal "black body" than does a coating wherein only zirconium is active as a pigment. The result is that for a given size of electrode and a given power dissipation the entire tube in which anodes thus coated are used operates at a lower temperature than those employing zirconium coatings of more conventional type. This fact results in improvements in operation which are not necessarily obvious upon first consideration. Vacuum tube structures are very commonly cylindrical and a relatively small portion of the heat energy developed within the tube escapes at the end of the cylinders. The greater part of the energy must be dissipated in a generally radial direction. Effectively the anode of the tube becomes an oven. The fact that it must dissipate, primarily by radiation, the heat energy developed by the impact of the electron stream upon the anode structure itself is obvious and is generally recognized. Heat must also be dissipated from other electrode structures within the tube. So far as the thermionic cathode is concerned this is undesirable; the less heat dissipated from this electrode the better, as any heat so lost must be made up by externally supplied energy. In power tubes, however, particularly in circuits where grid electrodes must be maintained at positive potentials for all or part of the cycle of operation, heating of such grid elements occurs owing both to electron bombardment and to absorption of energy radiated from other electrodes. In tubes of this class the grid temperatures may rise to a point where thermionic emission occurs and it is quite usual to form such grids out of materials treated with coatings which inhibit thermo emission of electrons. It is well known that thermionic emission increases very rapidly with increase in temperature; at ordinary room temperature such emission is so slight as to be entirely negligible, but above some threshold value, characteristic of the surface, electron emission increases at an accelerating rate. Reduction of temperature in grid structures by conduction is so small as to be negligible. The primary cooling effect must be by radiation to the surrounding anode structure and thence re-radiation from the anode through the walls of the tube.

Increase in the coefficient of radiation of the anode surface greatly increases dissipation of this type. No net loss of heat from the grid structure to the anode can occur unless the latter be at a lower temperature than the grid. Since the coefficients of radiation and absorption are identi-

cal, a high radiation coefficient of the anode surface facilitates heat transfer in this manner, increasing both the absorption from the grid structure and the ultimate radiation. The temperature gradient between the hot cathode and the exterior of the tube is thus increased.

With the coating of this invention this latter effect is so marked as materially to reduce primary emission of thermionic electrons from the grids, in comparison with otherwise identical tubes using conventional zirconium coatings. This greatly increases the effectiveness of emission-inhibiting coatings utilized upon the grid structures. This effect is readily measurable and is at once noticeable in its effect on tube performance. Other effects of better radiation and cooler operation may become evident only as the result of life tests or under conditions where the tube is operated up to its ultimate capacity but these delayed results are also accomplished by the use of electrodes coated in accordance with the invention.

It has already been stated that the relative proportions of the two metals in the mixture of powders is not critical. The coefficient of emissivity of the molybdenum is materially higher than that of the zirconium and because of its great covering power some improvement in emissivity, and therefore reduction in operating temperature, is achieved with the addition of very minute quantities of molybdenum to the mixture. For very small molybdenum contents the increase in emissivity appears to be substantially linear. As the proportion of molybdenum is increased the rate of increase in emissivity levels off, and above 50 percent of molybdenum the decrease in the amount of zirconium, and hence in the gettering action, becomes of greater moment than does the increased radiation. A marked improvement in emissivity is obtained with 15 percent of molybdenum and 85 percent of zirconium. This can be taken as about the upper limit of the linear improvement in emissivity with increase in molybdenum, although it should be noted that owing to the difficulties of accurate measurement as well as the gradual appearance of curvature in the characteristic this value is only approximate. Above 40 percent of molybdenum and 60 percent zirconium the flattening out of the curve has become quite definite and the preferred value of molybdenum content lies between these ranges. By continued experiment the range between 20 and 25 percent of molybdenum has been adopted in practice as the most advantageous, and the formula given above, using a zirconium content of 78 percent and a molybdenum content of 22 percent, is the one which is now used commercially.

Although the manufacture of the electrodes has been described with the use of a silica binder, electrodes have been successfully processed and operated wherein the binder used consisted of a pyroxylin lacquer. In so far as the gettering action and the increased emissivity are concerned very little difference is noted as between the coatings thus formed and those wherein the silica binder is used but the coating is not as adherent and therefore the silicate is preferred. Moreover, it is difficult to tell to what extent the overall improvement in emissivity is due to a better thermal bond between the coating and the base and what to a higher coefficient of emissivity. A loosening of the coating without actual flaking would destroy the effectiveness of the bond. Therefore, although the tendency of pyroxylin

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bonded coatings to flake off is not so pronounced as to affect more than a small percentage of electrodes so bonded, conservative design indicates the use of the binders giving the better bond and the more adherent coating. Nonetheless pyroxylin bonded coatings are deemed to be within the scope of this invention.

What is claimed is:

1. An electrode for thermionic vacuum tubes comprising a base of molybdenum and a radiating and gettering coating on said base consisting essentially of a mixture of zirconium and molybdenum powders secured to said base by an adhesive binder, the proportion of zirconium in said mixture being at least fifty percent by weight and the proportion of molybdenum being sufficient to form a coating having a radiant emis-

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sivity materially greater than that of a coating consisting essentially of zirconium powder in a binder.

2. An electrode in accordance with claim 1 wherein the proportion of zirconium in said mixture is between sixty percent and eighty-five percent by weight.

3. An electrode in accordance with claim 1 wherein the proportion of zirconium in said mixture is between seventy-five percent and eighty percent by weight.

References Cited in the file of this patent

UNITED STATES PATENTS

15	Number	Name	Date
	2,368,060	Wooten	Jan. 23, 1945
	2,536,673	Widell	Jan. 2, 1951